

VIVEKANANDA COLLEGE  
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KOLKATA-700063

NAAC ACCREDITED 'A' GRADE

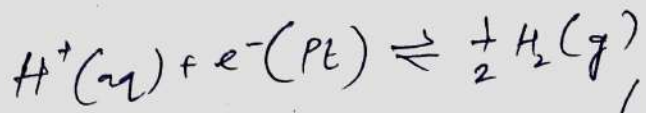


Topic:	Non Ideal Solutions
Course Title:	General Physical Chemistry
Paper:	BCMA CC3
Unit:	Non Ideal Solutions and Thermodynamics of EMF of cells
Semester:	2
Name of the Teacher:	<b>Dr. Subharthi Banerjee</b>
Name of the Department:	Biochemistry

• Gas-ion half cell  $\rightarrow$

eg. hydrogen gas-hydrogen ion  $\frac{1}{2}$  cell

Purified  $H_2(g)$  passed over Pt electrode dipped in an acidic solution

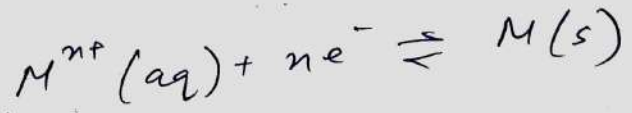


$$E_{H^+|H_2|Pt} = E_{H^+|H_2|Pt}^{\circ} - \frac{RT}{F} \ln \frac{(f_{H_2(g)} / f^{\circ})^{1/2}}{a_{H^+}} \quad [n=1]$$

• Metal-metal ion half cell  $\rightarrow$

Consists of a metal electrode dipped in a solution of  $M^{n+}$  ions.

eg. Zn-Zn<sup>2+</sup>, Cu-Cu<sup>2+</sup>, etc.



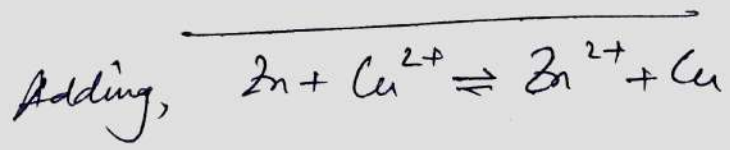
$$E_{M^{n+}|M} = E_{M^{n+}|M}^{\circ} - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}} \quad [a_{M(s)} = 1]$$

• Cell Reactions  $\rightarrow$



LH  $\frac{1}{2}$  cell:  $Zn \rightarrow Zn^{2+} + 2e^-$   $E_{Zn^{2+}|Zn} = E_{Zn^{2+}|Zn}^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{Zn^{2+}}}$

RH  $\frac{1}{2}$  cell:  $Cu^{2+} + 2e^- \rightarrow Cu$   $E_{Cu^{2+}|Cu} = E_{Cu^{2+}|Cu}^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{2+}}}$



$$E_{\text{cell}_1} = E_R - E_L$$

$$= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$= \left[ E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} \right] - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$\Rightarrow \boxed{E_{\text{cell}_1} = E_{\text{cell}_1}^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}}$$

For the cell,  $\text{Cu}|\text{Cu}^{2+}||\text{Zn}^{2+}|\text{Zn}$ ,

$$\boxed{E_{\text{cell}_2} = E_{\text{cell}_2}^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Zn}^{2+}}}}$$

Obviously,  $E_{\text{cell}_2} = -E_{\text{cell}_1}$

and cell reaction = Reduction at RHE - Oxidation at LHE

Generally,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \left\{ \prod_i (a_i)^{\nu_i} \right\}$$

$n \rightarrow$  no. of  $e^-$  involved

$\nu_i \rightarrow$  stoichiometry of the species

$$\text{and } E_{\text{cell}}^{\circ} = E_R^{\circ} - E_L^{\circ}$$

$\downarrow$   
standard reduction potential

The amount of work involved in moving  $n$  no. of electrons from the left hand half cell to the right hand half cell is

$$W = -nF[E_R - E_L] = -nF E_{\text{cell}}$$

where  $F = 96500 \text{ C mol}^{-1}$  (Faraday)

and  $\Delta G = -nF E_{\text{cell}}$

ie.  $\Delta G$  and  $E_{\text{cell}}$  have opposite signs.

$\Delta G$	$E_{\text{cell}}$	Nature of reaction
$\ominus$	$\oplus$	Spontaneous
$\oplus$	$\ominus$	Non-spontaneous
0	0	Equilibrium

⇒ For the general rxn:  $M^{n+} + ne^- \rightleftharpoons M$

$$E = E_{M^{n+}/M}^0 - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}}$$

ie.  $E_{M^{n+}/M}$  increases as  $a_{M^{n+}}$  increases & vice-versa.

→ For 10 times decrease in  $a_{M^{n+}}$ , there is  $\frac{0.0592}{n}$  volt decrease in the reduction potential.

For  $n=1$ ,  $E$  decreases by  $0.0592 \text{ V}$  for 10 times decrease in  $a_{M^{n+}}$ .

$n=2$ ,  $E$  decreases by  $\frac{0.0592}{2} \text{ V}$  or  $0.0296 \text{ V}$

⇒ Determination of thermodynamic data:

$$\Delta G = -nFE_{\text{cell}} \Rightarrow \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = -nF \left( \frac{\partial E}{\partial T} \right)_P$$

Again, from Gibbs Helmholtz eq.

$$\Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P$$

Temp. coeff. of  
E

$$\Rightarrow -nFE = \Delta H - nFT \left( \frac{\partial E}{\partial T} \right)_P$$

$$\Rightarrow \Delta H = -nF \left[ E - T \left( \frac{\partial E}{\partial T} \right)_P \right] \quad (1)$$

Unit of  $\Delta H$ : volt-coulomb [same as joule unit]

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} = nF \left( \frac{\partial E}{\partial T} \right)_P \quad (2)$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -nFE_{\text{cell}}^\circ \quad [\text{under standard conditions}]$$

$$\Rightarrow E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K_{\text{eq}} = \frac{2.303 RT}{nF} \log K_{\text{eq}} \quad (3)$$

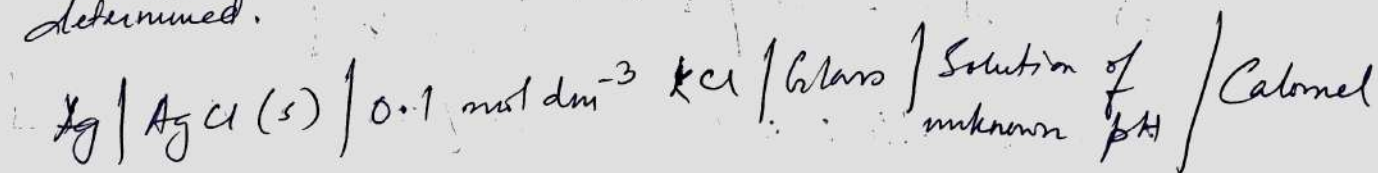
At 298K,

$$E_{\text{cell}}^\circ = \left( \frac{0.0592 \text{ V}}{n} \right) \log K_{\text{eq}} \quad (4)$$

⇒ Glass electrode:

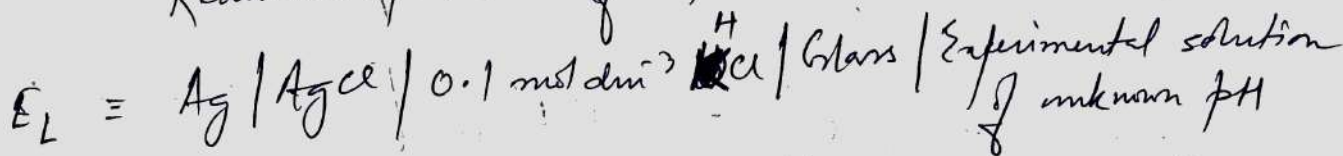
Consists of a special glass tube of relatively low melting point and high electrical conductance. The bulb contains a solution of constant  $H^+$  ion concentration and an electrode of definite potential.

Usually, Ag-AgCl electrode dipped in  $0.1 \text{ mol dm}^{-3}$  HCl solution or a Pt wire inserted in a pH 4.0 buffer containing a small quantity of quinhydrone. The bulb is inserted into a solution whose pH is to be determined.



$$E_{\text{cell}} = E_R - E_L$$

↓  
Reduction potential of ref. electrode



$$E_{\text{glass}} = E^{\circ}_{\text{glass}} - \frac{RT}{F} \ln a_{H^+} \quad a_{H^+} \rightarrow \text{activity of } H^+ \text{ ions in experimental solution}$$

$$E_{\text{glass}} = E^{\circ}_{\text{glass}} + \frac{2.303 RT}{F} \text{pH}$$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$= E_{\text{calomel}} - E^{\circ}_{\text{glass}} - \frac{2.303 RT}{F} \text{pH}$$

$$\text{At pH} = 7, E^{\circ}_{\text{glass}} = 0.062 \text{ V}$$

Components: (Tube within a tube)

A bulb ~~is~~ made from a specific glass

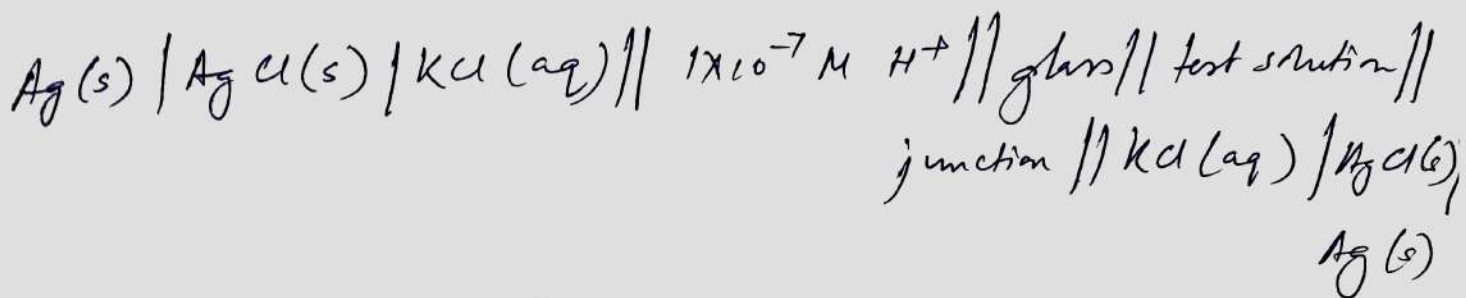
internal electrode  $\text{Ag}/\text{AgCl}$  or calomel

internal solution  $\text{pH} = 7$  of  $0.1 \text{ mol dm}^{-3} \text{ KCl}$

reference electrode (same as internal electrode)

reference solution ( $0.1 \text{ mol/L KCl}$ )

Inner tube contains an unchanging  $1 \times 10^{-7} \text{ mol dm}^{-3} \text{ HCl}$  solution.



$$\Delta G = \Delta G^\circ + RT \ln Q \quad Q \rightarrow \text{reaction quotient}$$

$$\Delta G^\circ = -nFE^\circ \quad \text{and} \quad \Delta G = -nFE$$

$$\Rightarrow -nFE = -nFE^\circ + RT \ln Q$$

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT \times 2.303}{nF} \log Q$$

$$\Rightarrow \boxed{E = E^\circ - \frac{0.0592}{n} \log Q}$$

$$\text{eg } A + n e^- \rightleftharpoons A^{n-} \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[A^{n-}]}{[A]}$$